POLYMERCAPTALS FROM ALDEHYDES AND DIMERCAPTANS

BY

ELIZABETH HENG HUI SHEN

B.S., St. John's University, 1945
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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Introduction

The recognition of the importance of polymer science in industry during the past twenty years had led many chemists to the investigation of these substances. Different polymers have been prepared by various methods in an attempt to find new and useful compounds from simple raw materials.

Polymers of promising qualities have been prepared from dithiols and diolefins since 1944 (1). The present study of the polymerization of dithiols with carbonyls was undertaken in an effort to add to the knowledge already accumulated regarding the dithiol polymers.

Discussion of Results

Polymercaptals (or polymercaptols) have been prepared by passing dry hydrogen chloride gas through a cold mixture of aldehydes (or ketones) and dithiols in the presence or absence of dioxane solvent. The polymers prepared have molecular weights ranging from 1,100 to 75,000, calculated from the intrinsic viscosities in benzene or chloroform solution.

The percentage conversion, based upon the original weight of dithiol was found by amperometric titration with silver nitrate, and ranged from 45 to 99 per cent.

The polymers have thiol end groups as shown by infrared absorption data, amperometric titration data and the fact that oxidation gives disulfide linkages. The absence of hydroxyl absorption in most of the infrared absorption curves indicates that hydroxyl groups are not present as end groups in these polymers.

The polymercaptals of benzaldehyde decamethylenedithiol, vanillin hexamethylene- and decamethylene- dithiols, were shown to have crystalline structures by X-ray diffraction patterns.

Oxidation of mercaptan sulfur to disulfide linkage by iodine in alkaline solution and of sulfur groups to sulfone by permanganate in acid solution has increased the intrinsic viscosity and melting point of these polymers.

Polymercaptals have been prepared from decamethylenedithiol

and the following carbonyl compounds: benzaldehyde, butyraldehyde, acetaldehyde, vanillin, and *m*-nitrobenzaldehyde.

Polymercaptols and polymercaptals have been prepared from hexamethylenedithiol and the following carbonyl compounds: benzaldehyde, butyraldehyde, acetaldehyde, vanillin, *m*-nitrobenzaldehyde, anisaldehyde, *p*-nitrobenzaldehyde, *p*-bromobenzaldehyde, acetophenone, *2*-butanone, *3*-methyl-*2*-pentanone, *4*-methyl-*2*-pentanone and cyclohexanone.

BIBLIOGRAPHY

1. Coffman, U. S. 2,347,182, April 25, 1944. Chem. Abs., 39, 226 (1945).

VITA

The author was born in Shanghai, China, on February 24, 1924. She attended McTyiere primary and high schools in Shanghai. She entered St. John's University in September, 1941, and received the degree of Bachelor of Science with honors in chemistry in January, 1945. Having secured the highest average in the school of science for the academic year of 1944-45, she was awarded "The Best in Science" prize in June, 1945. She enrolled in the graduate school at the University of Illinois in September, 1946, and received the degree of Master of Science in 1947. Since July, 1947, she has held a Special Research Assistantship in Chemistry on the Rubber Research Program, Rubber Reserve, Reconstruction Finance Corporation.

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